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(54) Title: SYNTHESIS OF SILICON NANOPARTICLES AND METAL-CENTERED SILICON NANOPARTICLES AND AP-
PLICATIONS THEREOF

(57) Abstract: IPCicon nanoparticles and metal-centered silicon nanoparticles and solution phase methods of synthesis using com-
monly available reagents and ordinary conditions. Solvent may be diglyme, triglyme, tetraglyme, even in mixture with nonpolar
solvent. A halosilane is reduced with metal, for example, at reflux conditions. Reaction product is hydrolyzed or passivated to
produce stable subunit that can agglomerate or polymerize into larger structures. Particle size synthesized can be controlled. These
particles and structures are photoluminescent and suitable for various applications, including light emitting devices.

Synthesis of Silicon Nanoparticles and Metal-Centered Silicon Nanoparticles and Applications Thereof

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CROSS REFERENCE TO RELATED APPLICATIONS

This nonprovisional application claims priority under 35 U.S.C. 119 (e) to U.S. provisional Application No. 60/150,240 filed August 23, 1999.

10 Background of the Invention

Field of the Invention

The present invention relates to silicon nanoparticles generally and methods of synthesis. More particularly, the present invention relates to silicon nanoparticles, metal-centered silicon (M@Si) nanoparticles and their derivatives and solution
15 phase methods of synthesis thereof.

Description of the Related Art

Silicon-based thin films have acquired a strategic position in materials science and technology due to their wide spectrum of applications. In particular is the tremendous interest in developing Si-based optoelectronic devices that can be
20 readily integrated with existing Si-based microelectronics technology. For example, integrating an entire optical system on a single chip offers many advantages, including small sizes, light weights, more functionality and elimination of intermediate packaging and assembly steps.

The discovery in 1990 of the strong visible photoluminescence (PL) at room
25 temperature of porous Si (PSi) [L.T. Canham, "Silicon Quantum Wire Array Fabrication by Electrochemical and Chemical Dissolution of Wafers" *Appl. Phys. Lett.*, 1990. 57: p. 1046], formed by electrochemically etching Si wafers in a HF solution, has rekindled the interest in Si-based light emitting devices (LEDs). There is now a considerable effort aimed at using PSi to fabricate practical LEDs [P. M.
30 Fauchet, "The Integration of Nanoscale Porous Silicon Light Emitters: Materials Science, Properties, and Integration with Electronic Circuitry" *J Lumin.*, 1999. 80: p. 53]. For example, U.S. Patent 6,049,090 to Clark describes silicon particles having diameters of 10 nm or less used in a semiconductor host matrix for making

electroluminescent displays. U.S. Patent 6,005,707 to Berggren, et al. disclose optical devices comprising crystalline materials such as Group III-V, Group II-VI and IV semiconductor nanocrystals in a polymer. U.S. Patent 5,882,779 to Lawandy discloses CdS, CuCl, ZnSe and porous silicon for semiconductor nanocrystals for electroluminescent display materials.

PSi has been made in several different forms, all with the common feature of being composed of Si crystallites. The visible PL occurs in PSi when the Si crystallites are smaller than 4 nm in size. [R. A. Bley and S. M. Kauzlarich, "A Low-Temperature Solution Phase Route for the Synthesis of Silicon Nanoclusters" *Journal of the American Chemical Society*, 1996. 118: p. 12461] However, owing to its porous nature, PSi can be a fragile material with properties that are sensitive to the chemical species used to passivate the crystallite surfaces. Careful oxidation of PSi produces a more durable material having longer-lived reproducible PL properties than H passivated PSi [L. Tsybeskov, S. P. Duttagupta, and P. M. Fauchet, *Solid State Commun.*, 1995. 95: p. 429] and the PL of PSi can now be tuned to different regions of the visible spectrum. However, the heterogeneity of the Si crystallite sizes in conventionally made PSi causes the emission lines to have fairly broad widths. [P. M. Fauchet, "The Integration of Nanoscale Porous Silicon Light Emitters: Materials Science, Properties, and Integration with Electronic Circuitry" *J Lumin.*, 1999. 80: p. 53]

Great efforts have been devoted to producing these Si-based thin films, resulting in a large variety of techniques (plasma-assisted deposition, laser ablation deposition, etc.). The microcrystalline model for amorphous silicon films, which had been considered as a possible structure in the 1970's, has been replaced by the continuous random network model that is now the established structure. Silicon in cluster-assembled form is considered an artificial structure distinct from either the amorphous and crystalline configurations, and in particular, metal-centered silicon clusters, may lead to new building blocks for nanostructured silicon. Of particular interest is the large variety of metastable solids created by assembling such clusters.

It is expected that the electronic properties of metal-centered silicon clusters contrast sharply with other types of nanoparticles, such as the quantum-dot quantum

well (QDQW) structures, recently exemplified by particles with a CdS (E_{gap} 2.5 eV and cubic $a=5.818$ Å) core surrounded by several monolayers of HgS (E_{gap} 0.5 eV and cubic $a=5.851$ Å) which is finally encapsulated with more layers of CdS. The larger CdS band gap confines the charge carriers within the HgS region, and avoids trapping of charge carriers at surface dangling bonds or defect sites. [A. Mews, A. V. Kadavanich, U. Banin, and A. P. Alivisatos, "Structural and Spectroscopic Investigations of CdS/HgS/CdS Quantum Dot Quantum Wells", *Phys. Rev. B*, 1996, **53**, p. R12342]. While the QDQW structures demonstrate that the electronic properties of a nanoparticle can be controlled, the QDQW paradigm does not characterize the electronic behavior of metal-centered silicon nanoclusters. More recent mechanisms proposed for PL from Si crystallites suggest the primary origin for the light emission is due to electron/hole recombination at surface states.

Previous workers have observed strong visible PL for both PSi and Si nanoclusters. [S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y.-H. Xie, F. M. Ross, Y. J. Chabal, T. D. Harris, L. E. Brus, W. L. Brown, E. E. Chablan, P. F. Szajowski, S. B. Christman, and P. H. Citrin, "Size, Shape, and Composition of Luminescent Species in Oxidized Si Nanocrystals and H-Passivated Porous Si" *Phys. Rev. B*, 1995. 52:p. 4910; G. R. Delgado, H. W. H. Lee, S. M. Kauzlarich, and R. A. Bley, "Comparative Optical Studies of Chemically Synthesized Silicon Nanocrystals" *Mat. Res. Symp. Proc.*, 1997. 452: p. 177] The large number of different experiments performed on these two chemical systems suggest they have a common mechanism responsible for the PL briefly discussed here. Essentially both systems contain an inner core of crystalline Si that can be passivated by a variety of surface adsorbates including H, O and organic groups. Much of the initial experimental data appeared to suggest the PL properties of the PSi were not very sensitive to the species used to passivate the surface, and from NEXAFS and IR spectra it has even been argued that H-passivated PSi surface is oxidized during the initial PL excitation without altering the PL emission. [S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y.-H. Xie, F. M. Ross, Y. J. Chabal, T. D. Harris, L. E. Brus, W. L. Brown, E. E. Chablan, P. F. Szajowski, S. B. Christman, and P. H. Citrin, "Size, Shape, and Composition of Luminescent Species in Oxidized Si Nanocrystals and H-Passivated Porous Si" *Phys. Rev. B*, 1995. 52:p. 4910] Although in oxygen-

free atmospheres, PSi can now be prepared with different porosities to produce stable PL ranging from red to blue in the visible spectrum. [H. Mizuno, H. Koyama, and N. Koshida, "Oxide-Free Blue Photoluminescence from Photochemically Etched Porous Silicon" *Appl. Phys. Lett.*, 1996. 69(25): p. 3779] Furthermore, since the visible PL only occurs when the Si crystallites are smaller than 4 nm in size [P. M. Fauchet and J. Von Gehren, "The Strong Visible Luminescence in Porous Silicon: Quantum Confinement not Oxide-Related Defects" *Phys. Stat. Sol. B*, 1997. 204: p. R7], these observations strongly support that PL originates from the radiative recombination of quantum-confined electrons and holes. [R. T. Collins, P. M. Fauchet, and M. A. Tischler, "Porous Silicon: From Luminescence to LEDs" *Phys. Today*, 1997. 50(1): p. 24] One consequence of the quantum confinement model, which has also been experimentally observed, [W. L. Wilson, P. F. Szajowski, and L. E. Brus, "Quantum Confinement in Size-Selected, Surface Oxidized Silicon Nanocrystals" *Science*, 1993. 262: p. 1242] is that the PL energy should increase with PSi porosity or as the Si nanocluster size becomes smaller. Unfortunately, reliably performing such experiments are challenging due to the difficulty of separating the Si nanoclusters into a very sharp and uniform distribution of particle sizes. The picture has been further complicated by the observation that after exposure to air PSi does not produce blue PL. As a consequence, some workers have suggested that the evidence for quantum size effects is weak and instead have proposed that the visible PL is due to surface effects or defects. One model, by Gole and coworkers and derived from quantum chemical calculations, has suggested that the ground and excited states associated with a silanone (Si=O) group at the crystallite surface can be correlated with the PL. [J. L. Gole and S. M. Prokes, "Resonantly Excited Photoluminescence from Porous Silicon and the Question of Bulk Phonon Replicates" *Phys. Rev. B*, 1998. 58: p. 4761] More recently, Wolkin et al. using tight binding calculations have proposed that quantum confinement and surface effects take place simultaneously. [M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, "Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen" *Phys. Rev. Lett.*, 1999. 82: p. 197] The H passivated PSi kept in an inert atmosphere shows a variation in the PL wavelength that is consistent with the quantum confinement model. For air exposed Si

crystallites with sizes above 3 nm, the PL wavelength is also consistent with quantum confinement, but for crystallite sizes below 3 nm the PL peak does not change significantly [S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y.-H. Xie, F. M. Ross, Y. J. Chabal, T. D. Harris, L. E. Brus, W. L. Brown, E. E. Chablan, P. F. Szajowski, S. B. Christman, and P. H. Citrin, "Size, Shape, and Composition of Luminescent Species in Oxidized Si Nanocrystals and H-Passivated Porous Si" *Phys. Rev. B*, 1995. 52:p. 4910] and surface effects involving primarily the Si=O bonds on the crystallite surface predominate. [M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, "Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen" *Phys. Rev. Lett.*, 1999. 82: p. 197] Wolkin *et al.*, like much of work done so far, have used PSi to test their model, but it is clearly desirable to have Si nanoparticles with well defined sizes and surface passivating groups to fully understand and hence better control PL. Passivation of the nanoparticles is useful to protect the structures from reactions with air or water.

However, apart from two examples of metal clusters being coated by silica, [A. N. Patil, R. P. Andres, and N. Otsuka, "Synthesis and Minimum Energy Structure of Novel Metal/Silica Clusters" *J. Phys. Chem.*, 1994. 98: p. 9247; L. M. Liz-Marzan, M. Giersig, and P. Mulvaney, "Synthesis of Nanosized Gold-Silica Core-Shell Particles" *Langmuir*, 1996.12: p. 4329] little previous effort to synthesize a metal centered silicon M@Si nanocluster appears. In fact, previous strategies for Si particle synthesis have focused on either the gas-phase pyrolysis of silanes [L. Brus, "Luminescence of Silicon Materials: Chains, Sheets, Nanocrystals, Nanowires, Microcrystals, and Porous Silicon" *J Phys. Chem.*, 1994. 98: p. 3575; L. Brus, "Luminescence of Silicon Nanocrystals and Porous Silicon" *Jpn. J Appl. Phys. Part 2 Lett.*, 1994. 34: p. 3; L. E. Brus, P. F. Szajowski, W. L. Wilson, T. D. Harris, S. Schuppler, and P. H. Citrin, "Electronic Spectroscopy and Photophysics of Silicon Nanocrystals: Relationship to Bulk C-Si and Porous Si" *J. Am. Chem. Soc.*, 1995. 117: p. 2915; L. Brus, "Chemical Approaches to Semiconductor Nanocrystals" *J Phys. Chem. Solids*, 1998. 59(4): p. 459; P. Li and K. Sattler, "Generation and Structural Analysis of Silicon Nanoparticles" in *Microcrystalline and Nanocrystalline Semiconductors*. 1995. San Francisco, CA: Materials Research Society; K. A. Littau, P. J. Szajowski, A. J. Muller, A. R. Kortan, and L. E. Brus, "A Luminescent Silicon

Nanocrystal Colloid via a High-Temperature Aerosol Reaction" *Journal of Physical Chemistry*, 1993. 97: p. 1224; S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y.-H. Xie, F. M. Ross, Y. J. Chabal, T. D. Harris, L. E. Brus, W. L. Brown, E. E. Chablan, P. F. Szajowski, S. B. Christman, and P. H. Citrin, "Size, Shape, and Composition of Luminescent Species in Oxidized Si Nanocrystals and H-Passivated Porous Si" *Phys. Rev. B*, 1995. 52:p. 4910; S. H. Tolbert, A. B. Herhold, L. E. Brus, and A. P. Alivisatos, "Pressure-Induced Structural Transformations in Si Nanocrystals: Surface and Shape Effects" *Physical Review Letters*, 1996. 76(23): p. 43 84; W. L. Wilson, P. F. Szajowski, and L. E. Brus, "Quantum Confinement in Size-Selected, Surface Oxidized Silicon Nanocrystals" *Science*, 1993. 262: p. 1242], exotic and highly reactive materials, [R. Heath, "A Liquid-Solution-Phase Synthesis of Crystalline Silicon" *Science*, 1992. 258: p. 1131; R. A. Bley and S. M. Kauzlarich, "A Low-Temperature Solution Phase Route for the Synthesis of Silicon Nanoclusters" *Journal of the American Chemical Society*, 1996. 118: p. 12461; C. S. Yang, S. M. Kauzlarich, H. W. H. Lee, and G. R. Delgado, "Synthesis and Characterization of Small Silicon Nanoclusters Terminated with Alkyls" *Abstr. Pap, Am. Chem. Soc.*, 1998. 216: p. 2; R. A. Bley and S. M. Kauzlarich, "A New Solution Phase Synthesis for Silicon Nanoclusters" *NATO ASI Ser. Partnership sub-series 3, High Technology*, 1996. 18: p. 467; G. R. Delgado, H. W. H. Lee, S. M. Kauzlarich, and R. A. Bley, "Comparative Optical Studies of Chemically Synthesized Silicon Nanocrystals" *Mat. Res. Symp. Proc.*, 1997. 452: p. 177] or procedures requiring high temperatures and pressures. [R. Heath, "A Liquid-Solution-Phase Synthesis of Crystalline Silicon" *Science*, 1992. 258: p. 1131] None of these approaches has proven capable of producing large quantities of Si nanoparticles in an economically feasible, environmentally friendly way, and only one method has resulted in size-selective synthesis. [R. Heath, "A Liquid-Solution-Phase Synthesis of Crystalline Silicon" *Science*, 1992. 258: p. 1131] JP 11014841-A-99 teaches synthesis of organosilicon nanoclusters having an overall elemental ratio $Si_xC_yH_zO_a$, where $0.1x < y < 10x$, $0.3x < z < 30x$ and $a = 0.5x$ using high energy sonication and magnesium metal. This application does not disclose particle sizes formed from disclosed synthesis.

- The atomic structure of Si particles has been roughly divided into three size ranges: small, medium, and large. In the small size range, lowest energy structures and cohesive energies for silicon clusters of size up to $n=10$ are well-established showing good agreement with the results from many theoretical groups. [M. Shen, "Raman Phonons of Silicon Wires" *Phys. Lett. A*, 1993. 180: p. 295; M. Menon and K. R. Subbaswamy, "Nonorthogonal Tight-Binding Molecular-Dynamics Study of Silicon Clusters" *Phys. Rev. B, Condens. matter*, 1993. 47(19): p. 12754; K. Raghavachari and C. Rohlfing, "Bonding and Stabilities of Small Silicon Clusters - a Theoretical-Study Of $\text{Si}_7\text{-Si}_{10}$ " *J Chem. Phys.*, 1988. 89(4): p. 16; K. Raghavachari, "Theoretical-Study of Small Silicon Clusters - Equilibrium Geometries and Electronic-Structures Of Si-2-7 , Si-10 " *J Chem. Phys.*, 1986. 84(10): p. 15; J. R. Chelikowsky, "Transition from Metallic to Covalent Structures in Silicon Clusters" *Phys. Rev. Lett.*, 1988. 60(25): p. 4; J. R. Chelikowsky, J. C. Phillips, M. Kamal, and M. Strauss, "Surface and Thermodynamic Interatomic Force Fields for Silicon Clusters and Bulk Phases" *Phys. Rev. Lett.*, 1989. 62(3): p. 292; J. R. Chelikowsky, K. M. Glassford, and J. C. Phillips, "Interatomic Force Fields for Silicon Microclusters" *Phys. Rev. B*, 1991. 44: p. 1538; P. Ballone, W. Andreoni, R. Car, and M. Parrinello, "Equilibrium Structures and Finite Temperature Properties of Silicon Microclusters from *ab initio* Molecular-Dynamics Calculations" *Phys. Rev. Lett.*, 1988. 60(4): p. 271; D. Tomanek and M. A. Schluter, "Calculation of Magic Numbers and the Stability of Small Si Clusters" *Phys. Rev. Lett.*, 1986. 56(10): p. 4; X. D. Jing, N. Troullier, D. Dean, N. Binggeli, J. R. Chelikowsky, K. Wu, and Y. Saad, "Ab-Initio Molecular-Dynamics Simulations of Si Clusters Using the Higher-Order Finite-Difference-Pseudopotential Method" *Phys. Rev. B Condens Matter*, 1994. 50(16): p. 4; N. Binggeli, J. L. Martins, and J. R. Chelikowsky, "Simulation of Si Clusters via Langevin Molecular Dynamics with Quantum Forces." *Phys. Rev. Lett.*, 1992. 68(19): p. 2956; O. F. Sankey, D. J. Niklewski, D. A. Drabold, and J. D. Dow, "Molecular-Dynamics Determination of Electronic and Vibrational- Spectra, and Equilibrium Structures of Small Si Clusters" *Phys. Rev. B Condens Matter*, 1990. 41(18): p. 10; C. M. Rohlfing and K. Raghavachari, "A Theoretical-Study of Small Silicon Clusters Using an Effective Core Potential" *Chem. Phys. Lett.*, 1990. 167(6): p. 7; K. Jackson, M. R. Pederson, D. Porezag, Z. Hajnal, and T. Frauenheim,

"Density-Functional-Based Predictions of Raman and IR Spectra for Small Si Clusters" *Phys. Rev. B*, 1997. 55(4): p. 2549] Raman vibrational spectra [E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, "Raman-Spectra of Size-Selected Silicon Clusters and Comparison with Calculated Structures" *Nature*, 1993. 366 (6450): p. 3] and infrared spectroscopy [S. Li, R. J. Van Zee, J. W. Weltner, and K. Raghavachari, "Si₃-Si₇. Experimental and Theoretical Infrared Spectra" *Chem. Phys. Lett.*, 1995. 243: p. 275] of silicon clusters give vibrational frequencies that agree very well with those predicted for the optimized structures. [E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, "Raman-Spectra of Size-Selected Silicon Clusters and Comparison with Calculated Structures" *Nature*, 1993. 366 (6450): p. 3] The most stable structures of small silicon clusters (less than ten atoms) are clearly of a metallic nature, as indicated by theoretical studies. In fact, the estimate is that for clusters of less than about 50 atoms, metallic structures are favored over covalent structures. [R. Chelikowsky, "Transition from Metallic to Covalent Structures in Silicon Clusters" *Phys. Rev. Lett.*, 1988. 60(25): p. 4] Thus, there is a critical size of $n=50$ for a metal-covalent phase transition. Other studies estimated this critical size for significant loss of metal character to occur in the range of 100-1000 silicon atoms. [D. Tomanek and M. A. Schluter, "Structure and Bonding of Small Semiconductor Clusters." *Phys. Rev. B*, 1987. 36: p. 1287]

In the medium size range ($N < 100$ atoms), theoretical arguments [D. Tomanek and M. A. Schluter, "Structure and Bonding of Small Semiconductor Clusters." *Phys. Rev. B*, 1987. 36: p. 1287; M. V. Ramakrishna and J. Pan, "Chemical-Reactions of Silicon Clusters" *J. Chem. Phys.*, 1994. 101(9): p. 11; E. Kaxiras, "Effect of Surface Reconstruction on Stability and Reactivity of Si Clusters" *Phys. Rev. Lett.*, 1990. 64 (5): p. 4; U. Rothlisberger, W. Andreoni, and M. Parrinello, "Structure of Nanoscale Silicon Clusters" *Phys. Rev. Lett.*, 1994. 72 (5): p. 665; D. A. Jelski, B. L. Swift, T. T. Rantala, X. Xia, and T. F. George, "Structure of the Si₄₅ Cluster" *J. Chem. Phys.*, 1991. 95: p. 8552; C. H. Patterson and R. P. Messmer, "Bonding and Structures in Silicon Clusters - a Valence-Bond Interpretation" *Phys. Rev. B Condens Matter*, 1990. 42(12): p. 26; T. Oshiro, C. K. Lutrus, D. E. Hagen, S. Beck, and S. H. S. Salk, "Quantal Estimates of Binding-Energies of Large Silicon Clusters (Si)_n With n -

- Greater-Than-10" *Solid State Commun.*, 1993. 87(9): p. 4; F. S. Khan and J. Q. Broughton, "Relaxation of Icosahedral-Cage Silicon Clusters via Tight-Binding Molecular-Dynamics" *Phys. Rev. B Condens Matter*, 1991. 43(14): p. 8; K. Kobayashi and S. Nagase, "A Theoretical-Study of the Stability of the Fullerene-Like Cage Structures of Silicon Clusters" *Bull. Chem. Soc. Jpn.*, 1993. 66: p. 3334] and experiments [E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, "Raman-Spectra of Size-Selected Silicon Clusters and Comparison with Calculated Structures" *Nature*, 1993. 366 (6450): p. 3; M. F. Jarrold, U. Ray, and M. Creegan, "Chemistry of Semiconductor Clusters: Large Silicon Clusters are Much Less Reactive towards Oxygen than the Bulk" *J. Chem. Phys.*, 1990. 93(1): p. 224; M. F. Jarrold and V. A. Constant, "Silicon Clusters Ions: Evidence for a Structural Transition" *Phys. Rev. Lett.*, 1991b. 67(21): p. 2994; J. L. Elkind, J. M. Alsord, F. D. Weiss, R. T. Laaksonen, and R. E. Smalley, *J. Chem. Phys.*, 1987. 87: p. 2397] indicate the existence of cage-like clusters, with surface reconstruction playing a decisive role in the particle's atomic structures. [E. Kaxiras, "Effect of Surface Reconstruction on Stability and Reactivity of Si Clusters" *Phys. Rev. Lett.*, 1990. 64 (5): p. 4; E. Kaxiras, "Surface-Reconstruction-Induced Geometries of Si Clusters" *Phys. Rev. B Condens Matter*, 1997. 56(20): p. 9; E. Kaxiras and K. Jackson, "Shape of Small Silicon Clusters" *Phys. Rev. Lett.*, 1993. 71(5): p. 4; E. Kaxiras and K. Jackson, "Structural Models for Intermediate-Sized Si Clusters" *Z. Phys. D Atoms Mol. Clusters*, 1993. 26(1-4): p. 3] Other models are also proposed for silicon clusters in the medium size range. Some of them predict compact sp^3 hybridized structures without five-membered rings [J. F. Sadoc and R. Mosseri, "Order and Disorder in Amorphous, Tetrahedrally Coordinated Semiconductor: A Curved-Space Description" *Philos. Mag. B*, 1982. 45: p. 467; M. Kiernan, "Curved Crystals, Defects and Disorder" *Adv. Phys.*, 1989. 38: p. 605] or structures based on usual crystalline forms (diamond and hcp). [H. J. Nolte and K. Jug, "Comparison of Size Effects in Aluminum and Silicon Clusters" *J. Chem. Phys.*, 1990. 93: p. 2584; K. D. Rinne and M. L. Mandich, *Phys. Rev. Lett.*, 1992. 69: p. 1823; H. Kupka and K. Jug, "Clusters as Crystal Fragments of Silicon Bulk" *Chem. Phys.*, 1989. 130: p. 23; S. Saito, S. Ohnishi, and S. Sugano, "Structures and Magic Numbers of Group IV Microclusters Calculated by Use of an Anisotropic Model

Potential" *Phys. Rev. B*, 1986. 33: p. 7036] A torus-like structure with a stack of six benzeneic Si_6 -rings and three additional face capping silicon atoms forming the top of the torus have also been proposed. [D. A. Jelski, B. L. Swift, T. T. Rantala, X. Xia, and T. F. George, "Structure of the Si_{45} Cluster" *J Chem. Phys.*, 1991. 95: p. 8552; J. C. Phillips, "Morphology of Medium-Sized Silicon Clusters" *J Chem. Phys.*, 1988. 88: p. 2090]

For large clusters ($N \gg 500$ atoms), most of the models (except the benzenic route mentioned above) favor diamondoid structures. This result is consistent with many of the experimental studies on nanoporous silicon, [J. C. Vial and J. Derrien, Porous Silicon, Science and Technology. 1995, Heidelberg: Springer] and microcrystalline structures. [Z. Iqbal and S. Veprek, *J Phys. C*, 1982. 15: p. 377]

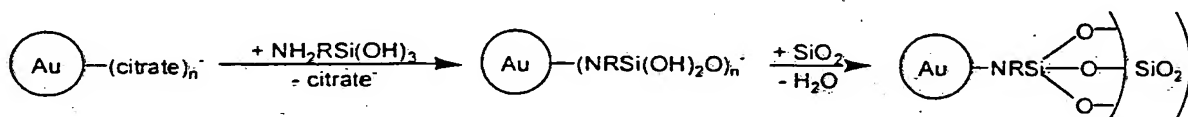
Small metal clusters formed either in the gas and solution phases have also attracted considerable interest. Even the small metal clusters that satisfy shell filling 'magic numbers' appear to form stable simple close-packed crystalline structures. [T. P. Martin, "Shells of Atoms" *Phys. Rep.*, 1996. 273: p. 199.] Such metal clusters can be further stabilized by surface adsorbates that do not strongly influence the clusters internal structure. [E. K. Parks, B. J. Winter, T. D. Klots, and S. R. Riley, "The Structure of Nickel Clusters" *J Chem. Phys.*, 1991. 94(3): p. 1882] In fact large surface adsorbates have been used to control size of Au nanoclusters formed in solution synthesis. [T. G. Schaaff, G. Knight, M. N. Shafigullin, R. F. Borkman, and R. L. Whetten, "Isolation and Selected Properties of a 10.4 kDa Gold:Glutathione Cluster Compound" *J Phys. Chem. B*, 1998. 102: p. 10643] A variety of methods has been developed for the synthesis of metal nanoclusters [G. Schmidt, "Large Clusters and Colloids. Metals in the Embryonic State" *Chem. Rev.*, 1992. 92: p. 1709] including metal ion implantation [P. Mazzoldi, G. W. Arnold, G. Battaglin, F. Gonella, and R. F. Haglund, "Metal Nanocluster Formation by Ion Implantation in Silicate Glasses: Nonlinear Optical Applications" *J. Nonlinear Opt. Phys. Mater.*, 1996. 5(2): p. 285; A. L. Stepanov, S. N. Abdullin, R. I. Khabullin, V. F. Valeev, Y. N. Osin, V. V. Bazarov, and I. B. Khaibullin. "Ion Synthesis of Colloidal Silver Nanoclusters in the Organic Substrate" in *Thin Films for Integrated Optics Applications*. 1995. San Francisco, CA: Materials Research Society], sol-gel synthesis of materials containing metal nanoclusters [L. Armelao, R. Bertoncello,

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Micelle/Sol-Gel Synthesis" *Chem. Mater.*, 1997. 9(2): p. 423; D. V. Leff, P. C. Ohara, J. R. Heath, and W. M. Gelbart, "Thermodynamic Control of Gold Nanocrystal Size: Experiment and Theory" *J Phys. Chem.*, 1995. 99: p. 7036; I. Lisiecki and M. P. Pileni, "Synthesis of Copper Metallic Clusters Using Reverse Micelles as Microreactors" *J Am. Chem. Soc.*, 1993.115: p. 3887; J. P. Wilcoxon, T. Martino, E. Klavetter, and A. P. Sylwester. "Synthesis and Catalytic Properties of Metal and Semiconductor Nanoclusters" in *Nanophase Materials: Synthesis-Properties-Applications*. 1994. Corfu, Greece: Kluwer Academic Publishers].

Synthesis of metal centered nanoclusters coated by an outer silicon-containing layer has been reported by only two groups, each utilizing substantially different methods. In the first method, gold colloids were homogeneously coated with silica using a silane coupling agent as a primer to render the gold surface vitreophilic (Scheme 1). [L. M. Liz-Marzan, M. Giersig, and P. Mulvaney, "Synthesis of Nanosized Gold-Silica Core-Shell Particles" *Langmuir*, 1996.12: p. 4329]. Variation of the silica shell thickness and the refractive index of the solvent allowed the investigators to control of the optical properties of dispersions of the resulting silica-coated particles. This solution phase synthesis allowed production of the desired compound in macroscopic quantities paving the way for practical applications.



Scheme 1

In the second method, heteronuclear clusters of metal/silica were synthesized via gas-phase aggregation. This method resulted in metal nanoclusters that were directly encapsulated in a silica coat without utilizing a coupling reagent. Although this method was useful in the preparation of particles with gold, silver and Cu₂O cores, only microscopic quantities of the desired product were formed. [A. N. Patil, R. P. Andres, and N. Otsuka, "Synthesis and Minimum Energy Structure of Novel Metal/Silica Clusters" *J. Phys. Chem.*, 1994. 98: p. 9247] In both cases the metal substrate is coated in silica as opposed to silicon.

It would therefore be desirable to have methods using common reagents and routine reaction conditions for synthesizing silicon nanoparticles. It would also be desirable to have methods for synthesizing silicon nanoparticles by which particle size distribution and composition can be easily controlled.

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Summary of the Present Invention

The present invention addresses these and other problems and disadvantages by providing novel methods of synthesis and novel Si -based compositions suitable for numerous applications, including in optoelectronics and biological applications.

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Thus, according to one embodiment, the present invention is directed to multi-step solution phase methods for preparing silicon-containing particles. For example, a halosilane can be reduced with a metal under reflux in a solvent to form a first reaction mixture containing a metal halide, amorphous silicon and halogenated silicon nanoparticles. The first reaction mixture may then be permitted to stand for a sufficient time to form a second reaction mixture including larger particles based on the halogenated silicon nanoparticles. The larger particles formed may then be hydrolyzed with water to form a third reaction mixture containing a haloacid and hydrolyzed silicon nanoparticles. Alternatively, the larger particles formed may be passivated with an organic Grignard reagent to form a fourth reaction mixture including a metal halide salt and organic passivated silicon nanoparticles.

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According to some aspects of the invention, these Si-based nanoparticles are prepared by solution phase methods enabling "large quantities" (on the order of grams) of size-selected particles to be produced. Particle size selection, e.g., particle diameter of less than 100 nm, or between about 0.5-10 nm, is controlled both by the kinetics of the synthesis and by solution phase separation techniques.

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According to another aspect, the present invention is directed to silicon-based nanoparticles and agglomeration of these nanoparticles prepared according to the solution phase methods described herein.

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The present invention also includes novel Si-based nanoparticle (e.g., Si and metal-centered Si nanoparticles) architectures for the manufacture of new LEDs.

The electronic properties of the Si-based nanoparticles provide a PL system with a more homogeneous composition than PSi making them suitable for use in numerous applications.

5 Brief Description of the Drawings

The present invention will be better understood by reference to the following figures in which like reference numerals refer to like elements and in which:

Figure 1 graphically illustrates an idealized structure of a $\text{Si}_{20}\text{OH}_{20}$ particle according to the invention.

10 Figure 2 is a graph presenting a typical experimental (corrected for Mie scattering) and theoretical UV/Visible absorbance spectra for unfiltered $\text{Si}_{20}\text{OH}_{20}$ particles (and agglomerates thereof) according to the invention (24 hour reaction time and 24 hour development time).

Figure 3 is a photoluminescence spectrum for a reaction mixture achieved
15 from a method of the present invention.

Figures 4 and 5 are fluorescence emission spectra in water and glycerol, respectively, of silicon-based particles prepared according to a method according to the present invention.

Figures 6(a), (b) and (c) are photoluminescence spectra of a reaction mixture
20 achieved from a method of the present invention and selected fractions of smaller and larger particles therein, respectively.

Figure 7 is a TEM of silicon-based nanoparticles (about 4 nm) in a reaction mixture prepared according to the present invention.

Figure 8 is an *in situ* parallel electron energy loss spectrum (EELS),
25 confirming the particles according to the present invention were silicon nanoparticles.

Description of the Preferred Embodiments

The present invention provides photoluminescent Si-based nanoparticles and
30 solution phase synthetic methods to produce these particles in relatively large quantities and in the desired sizes. Applications of silicon nanoparticles and metal-centered silicon nanoparticles according to the invention have numerous and

diverse application, including microelectromechanical optical system devices, blue lasers, wavelength-division-multiplexing systems on a chip, and even biological applications.

The methods of the present invention are highly versatile and environmentally friendly since they avoid highly toxic materials such as HF and GaAs. In addition, methods of the present invention use commonly available reagents and ordinary reaction conditions.

At least five parameters of the methods according to the present invention may be changed to tailor the properties of the particles produced: the identity of the metal, the size of the metal cluster, the thickness of the silicon coating, solvent and the group used to passivate the surface of the cluster. Changes made to any of these factors can change the electronic and/or optical properties and/or size distribution of the material produced. Depending on the work function of the metal chosen, the particles will act as either n-doped or p-doped semiconductor particles. Variation in the ratio of metal atoms in the core to silicon atoms in the outer shell can fine-tune this characteristic, thereby making the doping more or less pronounced. The addition of electron withdrawing or electron-donating passivation groups can also affect the electronics. Additionally, the polarity of the passivation group affects the solubility of the particles in different solvent systems.

To assist with the understanding of the present invention, the following definitions are provided.

By the term "nanoparticles," it is meant particles in the nanometer size range (1-100 nm). Of special interest are particles having 0.5-10 nm diameters. The term "nanoparticle" is used herein interchangeably with the terms "particle", "cluster" and "nanocluster."

By the term M@Si or the phrase "metal-centered silicon particle," it is meant: a particle having a metal core surrounded by a silicon-containing layer. The metal M is an appropriate metal such as Cu, Ag, Au, Ni, Fe, etc. The layer surrounding the core may include crystalline Si. The outermost layer of the particle is a passivation layer composed of, for example, hydroxyl groups and methyl groups, depending on the compounds used for passivation. Transition metals are also suitable metals for the metal core in the particles according to the invention.

By the term "passivate," it is meant: to protect a structure against reaction with air or water. Discussed below are exemplary compounds that can be reacted with the intermediate particles prepared according to the present invention to achieve passivation.

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SYNTHESIS AND CHARACTERIZATION OF SI AND RELATED NANOCUSTER MATERIALS OF THE INVENTION

Silicon nanoparticles according to the invention generally are produced through simple reduction of silicon tetrachloride, SiCl_4 , or other suitable organohalosilane, RSiCl_x , by a metal such as sodium in solvent in an inert environment (Step 1). Under certain conditions, the product of the reaction appears to be $\text{Si}_{20}\text{Cl}_{20}$ that subsequently can combine with other $\text{Si}_{20}\text{Cl}_{20}$ species during the "developing time", if any, through reductive coupling, polymerization or other derivativization of the $\text{Si}_{20}\text{Cl}_{20}$ (or the product chlorosilane Si_mCl_n) species in the presence of the metal to form polymeric clusters or agglomerates of the intermediate $\text{Si}_{20}\text{Cl}_{20}$ species (Step 2). Polymerization can be quenched by either hydrolysis or by substitution of the chloro-groups with organo-groups such as methyl or butyl or even aryl groups. Hydrolysis is accomplished by adding water to the reaction mixture (Step 3a). Reaction of the parent chlorosilane with the corresponding Grignard reagent (RLi or R_2Mg) substitutes an organic group (Step 3b) to yield particles resembling hydrocarbons externally, but which maintain a silicon core. Thus, after hydrolysis or passivation, the resulting particle structure features Cl (or the particular halogen used) outermost, internal Si-Si bonds and reactive Si-Cl (or Si-halide) bonds. When exposed to water, OH displaces the Cl (or halide) in the Si-Cl (Si-halide) bonds. Generally, synthetic methods according to the invention include several steps, as shown below.

The first step is a solution phase reduction of a halosilane with metal in inert environment under reflux conditions to form a reaction mixture containing a metal halide, amorphous silicon and halogenated silicon nanoparticles. An example of this step reducing silicon tetrachloride with sodium metal is $\text{SiCl}_4 + \text{Na} \rightarrow \text{Si}_{20}\text{Cl}_{20} + \text{NaCl} + \text{amorphous silicon}$.

The halosilane can be SiCl_4 , SiHCl_3 , SiH_2Cl_2 , SiH_3Cl or corresponding silanes of other halogens, or an organohalosilane R_nSiCl_x (or corresponding organosilane of other halogens). R can be any organic group that can bond to Si, including alkyl or aryl groups. It is expected that sterically demanding R will affect the size of particles ultimately obtained. For example, large R groups may lead to the formation of particles with more narrow size distribution ranges. [Heath, J., "A Liquid-Solution Phase Synthesis of Crystalline Silicon", *Science*, 1992; 258; p. 1131; O. Itou, T. Miwa, M. Suzuki, and A. Watanabe, "Production of Organic Solvent Soluble Organosilicon Nanocluster", *Dialog.*, 1998, Hitachi Ltd. Japan.]

The reductant for this step can be any metal such as a Group I metal, Group II metal or transition metal.

Reaction conditions for Step 1 involve the addition of the reagents to a dry solvent using Schlenk line techniques and inert conditions. The solvent preferably coordinates with the individual particles to avoid or reduce agglomeration of particles at this point in the synthesis. In addition, the solvent should also have a relatively high boiling point compared to other solvents generally, though suitable solvents have relatively low boiling compared to the sintering temperatures used for conventional gas phase syntheses. Thus, a preferred solvent used in these studies was diglyme ($T_{bp} = 162^\circ\text{C}$) distilled from sodium under inert conditions prior to use. Other solvents that were tried included tetrahydrofuran (THF, $T_{bp} = 66^\circ\text{C}$), diethyl ether ($T_{bp} = 34.5^\circ\text{C}$), triglyme ($T_{bp} = 216^\circ\text{C}$) and tetraglyme ($T_{bp} = 276^\circ\text{C}$). Presumably because of their relatively low boiling points (compared to sintering temperatures, e.g., on the order of $600\text{-}1000^\circ\text{C}$), the use of THF or diethyl ether did not result only in the formation of amorphous silicon. Triglyme and tetraglyme yielded similar results to those obtained by using diglyme; however, the removal of these solvents proved tedious and difficult without yielding significantly higher yields. Distribution of particles created using the triglyme synthesis differs from that achieved from the diglyme synthesis, as indicated by a shifted photoluminescence spectrum and differing line shape. Solvent mixtures may also be suitable media for carrying out methods according to the present invention. Thus, for example, diglyme may be diluted with a less polar solvent, e.g., hexane, adjusting the polarity of diglyme and the solubility of various species therein.

In the first step, the reactants preferably were refluxed with constant stirring (using a magnetic stirbar) for a period of 24 hours. Efficient stirring was found to be critical to this step. If stirring stopped or was inefficient, the reaction resulted only in the formation of amorphous silicon. If stirring is maintained, the combined yield of $\text{Si}_{20}\text{Cl}_{20}$ and its polymeric derivatives was found to be approximately 10 %. Faster stirring appeared to favor formation of relatively smaller particles, while slower stirring appeared to favor larger agglomerates forming. Eventually, these larger agglomerates would be expected to form amorphous silicon. It is also noted that relatively higher halosilane concentrations tends to favor the formation of agglomerates.

The reduction could probably be run at temperatures less than the reflux temperature for the solvent used. It is noted that the reduction reaction begins immediately upon addition, at room temperature, of the reagents when diglyme, triglyme or tetraglyme is used as a solvent. At temperatures substantially lower than the reflux temperature, it may be expected that the reduction will take significantly longer than at reflux conditions and that these conditions may favor larger agglomerates forming.

A "developing time" (Step 2) can follow the reduction step. Immediate hydrolysis (Step 3a) after reduction, that is, no "development time" (no Step 2), resulted in the formation of small silicon hydroxide clusters, believed to be $\text{Si}_{20}(\text{OH})_{20}$ monomer. If the reaction mixture after the initial reduction is complete is allowed to stand for a period of time but prior to quenching (Step 3), larger clusters of the $\text{Si}_{20}(\text{OH})_{20}$ subunit(s) formed in step 1 result. This "development time" (Step 2) achieves the particle size control that is an especially important advantage of the present invention compared to conventional syntheses. Generally, longer development times will produce larger particles. These larger species are covalently bound and do not break up into smaller species under physical duress such as sonication.

In step 3a, water was added to hydrolyze the $\text{Si}_{20}\text{Cl}_{20}$ intermediates. In step 3b, the identity of the organolithium reagent, as well as its stoichiometry with respect to the silicon cluster, can be varied in order to change the polarity and electronics of the clusters.

In the present work, the initial reduction time (with reflux conditions) was 24 hours, and the following developing time was also 24 hours (total = 48 hours). Periods longer than 24 hours for developing time may be used. Generally, "development time" is too long when precipitation occurs, e.g., formation of colloid leading to particles dropping out of solution.

At the end of the desired developing time, the samples were quenched either by hydrolysis (Step 3a) or by reaction with a Grignard reagent (Step 3b). Solvent was removed following either step 3a or step 3b and then the particles were filtered or separated according to size.

Following the synthesis reactions, physical separation of nanoclusters into specific and narrow size distribution ranges is possible using conventional techniques, such as ultra filtration. In this method, a solution of the product particles was passed through successive filters of decreasing nominal pore size. Larger particles were retained on the first filters while smaller particles pass through the first filters and were retained upon later filters. When desired, further separation was obtained by using size-selective precipitation (SSP) and size-exclusion high performance liquid chromatography (HPLC). SSP was accomplished by adding a miscible 'nonsolvent' to a solution containing nanoclusters of varying size. The nonsolvent (i.e., that in which the clusters are not soluble but was miscible with the solvent) may be added until agglomeration of the particles is observed. The solid particles may then be separated by high-speed centrifugation. Larger nanocrystals agglomerate first presumably due to their greater van der Waals attraction. SSP or HPLC can be used instead of ultrafiltration or in addition to it.

By iteration of precipitation and centrifugation, fractions of narrow size distribution can be produced. Further reduction of size variance is accomplished by subsequent size-exclusion HPLC. The precipitation process is reversible, allowing nanoclusters to be redissolved in their original solvent and while maintaining their physical properties.

An exemplary synthesis is now described. Each step preceding the addition of water was conducted in an inert atmosphere (nitrogen gas). Diglyme (~20 mL) was freshly distilled from sodium metal under nitrogen and was added to a clean, dry Schlenk flask (100 mL). To the flask was added silicon tetrachloride (4.0 mL):

mmol), sodium metal (3.274 g: 142.4 mmol), and a magnetic stirbar. The mixture was stirred and heated at reflux for a period of 24 hours after which the solution was observed to luminesce when irradiated with a hand-held UV lamp (irradiation ~365 nm). The flask was cooled in an ice bath and a solution of methyl lithium was slowly added via syringe (28 mL of a 1.4 M tetrahydrofuran solution: 39 mmol). The solution was once again heated at reflux for two hours and subsequently cooled to room temperature. Water (20 mL: 1.1 mol) was slowly added with no apparent reaction. The mixture was filtered through a 0.45 filter and the solids discarded. The filtrate was then sequentially passed through a series of Amicon™ ultrafiltration membranes: YM10 → YM3 → YM1 → YC05. Each time the membrane was flushed with water while stirring the filtration chamber vigorously in order to ensure that all of the water-soluble by-products of the reaction (salts and hydroxides), and the smallest particles were washed through the membranes retaining only the particles larger than the pore size of the membrane. After the filtration was completed, the nanoparticles were washed off of the top of each of the membranes with the largest particles being recovered from the YM10 membrane, and the smallest particles being recovered from the YC05 membrane. In this way, the particles were selectively separated on the basis of size.

Figure 1 provides a graphic illustration of an idealized structure of a $\text{Si}_{20}(\text{OH})_{20}$ particle, believed to be formed by the reduction step described above.

Figure 2 provides an overlay of a theoretical UV/visible spectrum for a $\text{Si}_{20}(\text{OH})_{20}$ particle (based on the idealized structure of Figure 1) and an observed spectrum for silicon nanoparticles according to the present invention. When excited by ultraviolet radiation (280, 310, 340, 370, 400 nm), the particles emit light in the UV and visible regions (300-500 nm). For each wavelength used, excitation of specific populations corresponding to different particle sizes is observed. Excitation of wavelengths above 365 nm or below 300 nm resulted in no new peaks, an observation correlating well with findings reported by Brus, Kauzlarich and others. [W. L. Wilson, P. F. Szajowski, and L. E. Brus, "Quantum Confinement in Size-Selected, Surface Oxidized Silicon Nanocrystals", *Science*, 1993; 262; p. 1242; G. R. Delgado, H.W. H. Lee, S. M. Kauzlarich, and R. A. Bley, "Comparative Optical Studies of Chemically Synthesized Silicon Nanocrystals", *Mat.Res.Symp.Proc.* 1997;

452; p. 177; S. V. Gaponenko, I. N. Germanenko, E. P. Petrov, "A. P. Stupak, V. P. Bondarenko, and A. M. Dorofeev, "Time-Resolved Spectroscopy of Visibly Emitting Porous Silicon", *Appl.Phys.Lett.*, 1994; **64** (1); p. 85; S.V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals*, 1998, N.Y., Cambridge University Press.]

5 As can be seen in Figure 2, good correlation exists between the theoretical and observed spectra. For the theoretical spectrum, the ground state geometry was optimized by semiempirical AM1 calculations, and the absorption spectrum was calculated with a singles only CI calculation using the ZINDO/S parameterization. Two hundred energy states were used. While a great deal of Mie scattering
10 appeared in the observed spectrum (curved baseline), peaks or shoulders were also observed indicating molecular absorptions. Models of the silicon hydroxide structure other than the $\text{Si}_{20}(\text{OH})_{20}$ model discussed herein may fit the data presented. Mass spectroscopy analyses are underway for more conclusive evidence of the identity of the species.

15 As the developing time increases (e.g., a longer time for standing at room temperature), a shift toward the red end of the spectrum was observed. This shift is most likely due to the formation of larger polymeric species based upon the $\text{Si}_{20}\text{Cl}_{20}$ subunit.

Figure 3 is a photoluminescence spectrum for a reaction mixture immediately
20 hydrolyzed after the reduction step according to the present invention. As can be seen, the spectrum indicates a narrow particle distribution with three species present, believed to be $\text{Si}_{20}(\text{OH})_{20}$ particle in a monomeric form, as well as dimers and trimers of the particle.

Further support for a distribution of particle sizes possible from the present
25 invention is given by the emission lifetime studies. Lifetimes were measured by a fluorescence lifetime machine for the species in the reaction solution using both water (Figure 4) and glycerol (Figure 5) as solvents. The data was fitted best using a four discrete lifetime system. Although Gaussian, Lorentzian, and bimodal Gaussian distributions were modeled, the χ^2 value for the four discrete lifetime system
30 was found to be lower by an order of magnitude. Of the four lifetimes shown, the shortest (both in the aqueous and glycerol systems) is attributed to scattering; however, the other three were most likely due to three different species in solution.

These species were most likely the monomer (about 30 ns), the dimer (about 11 ns), and the trimer (about 3 ns), although definitive assignments cannot be made from the lifetimes alone. The observed shift in lifetimes from water to glycerol indicated that the emission process was linked to surface states as opposed to quantum confinement. That is, the solvent must be interacting with the particles. This evidence further substantiated the proposed $\text{Si}_{20}(\text{OH})_{20}$ structure because, in this structure, all of the silicon atoms are located on the surface of the cluster as opposed to structures derived from porous silicon that have both interior and exterior silicon atoms.

All observed emissions were in the blue and UV portion of the spectrum. Consequently, these silicon nanoparticles could advantageously be used in a laser, LED or other light emitting device, obviating the need to resort to toxic materials such as GaAs or difficult reaction schemes.

After separation into distinct size-ranges, transmission electron microscopy (TEM) was used to calibrate particle sizes. Figure 7 displays a TEM image of particles in the 4 nm in size range (corresponding to PL spectrum Figure 6(b)). The TEM image of Figure 7 and the corresponding spectra of Figure 6 were obtained from particles that had passed through a YM10 membrane, but which were retained on a YM3 membrane. (In the Amicon literature, YM refers to membranes composed of regenerated cellulose. The numbers refer to the average cutoff value for the membrane with respect to solution-phase protein separations. A YM10 membrane has a 10,000 Dalton cutoff, while a YM3 has a 3,000 Dalton cutoff. The YC05 has a 500 Dalton cutoff.)

Separation of the bulk mixture using ultrafiltration resulted in the spectra shown in Figures 6(b) and (c). The spectra in 6(b) correspond to particles whose average diameter was approximately 4 nm, while those in 6(c) depict particles of less than 4 nm. Although these results contradict the traditional "particle in a sphere" model for Si nanoparticles [M. Nirmal, and L. Brus, "Luminescence Photophysics in Semiconductor Nanocrystals", *Acc.Chem.Res.*, 1999, 32: p. 407] (i.e., smaller should be bluer) the difference can most likely be explained by the presence of defects within the cluster and/or by surface effects.

For analysis of particle suspensions prepared according to the present invention, the measured sample spectra were normalized with a reference spectrum of the pure liquid. The UV-photoluminescence studies give an optical characterization of the particles.

5 In Figure 7, the grain in the background of the image is due to the carbon substrate. Scanning and transmission electron micrographs (SEM and TEM, respectively) of the products indicate particles ranging from 40 to less than 5 nm in diameter.

To confirm that the particles were silicon, an in situ parallel electron energy
10 loss spectrum (EELS) was also obtained (Figure 8). The sharp absorption edge for silicon can clearly be seen at 1834 eV. The reaction mixture was the same as that scanned for the TEM image of Figure 7.

Evidence for larger species (e.g., dimers of $\text{Si}_{20}(\text{OH})_{20}$) being created using methods according to the present invention is given by fluctuation correlation
15 spectroscopy (FCS). Using a 10 nM aqueous solution of fluorescein as a reference, FCS analysis of aqueous solutions of the reaction mixture indicated an average particle diameter of 2 nm. The theoretical diameter for $\text{Si}_{20}(\text{OH})_{20}$ is approximately 0.8 nm indicating that the predominant species present in the reaction mixture was the dimer, although it is believed that monomer and trimer species were also present
20 in the final reaction mixture (through step 3a) and with a 24 hour development time.

Spectral studies also imply a relationship between the initial reactant concentration and final particle size. For example, if the concentration of SiCl_4 is too high, the only product from the reduction/reflux step is amorphous silicon.

25 EXEMPLARY M@SI NANOPARTICLES SYNTHESIS

We have successfully prepared Cu and Fe-centered particles, Cu@Si and Fe@Si, respectively. These particles have distinct metal and silicon domains and should not be considered to be silicides (e.g., Na-Si). Perhaps a useful description of the particles is that of a fish eye with the metal core in the center surrounded by a
30 silicon shell. Physical and chemical characterizations are currently underway.

The metal core of M@Si, in addition to influencing the Si structure, may act as an electron/hole reservoir providing beneficial charging effects on the Si shell.

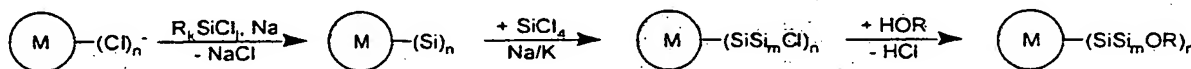
The flexibility of metal core choice, coupled with selection of appropriate passivating groups on the Si surface, should provide a useful range of parameters for the development of a nanoparticle with high EL efficiency.

All syntheses were performed in inert environments using standard glovebox and Schlenk techniques and similarly to the reaction scheme set forth above. Generally, metal clusters of distinct sizes were grown by the reduction of metal salts in organic solvents. Chelating ligands, e.g., polyammonium or polycarboxylic acid, added to the solvent before the reaction occurred solution, stabilizing smaller clusters by inhibiting aggregation. When the metal clusters were separated, e.g., using ultrafiltration techniques, into more narrow distributions of sizes prior to reduction, the final nanoparticle product sizes were more uniform. This uniformity led to enhanced particle stability and the ability to create specific clusters.

In addition to Cu and Fe, other metals include Au, Ag, and Ni. M@Si clusters containing Fe or Ni have the added advantage of being magnetic and may be used as actuators in nanomechanical devices. By adjusting the metal to silicon ratio in these clusters, the electronic properties of the clusters can be changed. The structural and electronic properties of M@Si materials are expected to be vastly different than those of the silica coated metal nanoclusters. The silicon adlayers, forming the outer shells, will probably bond to the metal cores creating some interesting structural entities, especially when the metal core has a large lattice mismatch with bulk crystalline Si.

Silicon was added to the outer surface of the metal cluster via the additions of a suitably substituted chlorosilane. Increased coating thickness should be achieved through the addition of SiCl_4 (or the organohalosilane used) in the presence of a reductant. Also, adjusting reaction times and reactant concentrations can control coating thickness.

In the final step, the particles were passivated by either simple oxidation or by the addition of an alcohol, an alkyl Grignard, or an aryl Grignard reagent.



Scheme 3.

Alternatively, M@Si nanoparticles can be synthesized without addition of a metal reductant as follows.

Metal clusters (e.g., Ag clusters) can be prepared from metal salts using well-known conventional techniques. The clusters are purified by removing the solvent and any reaction byproducts and then size selected using any of the techniques described above. The purified metal clusters of the desired size may then be reacted directly with a halosilane (e.g., SiCl_4) in a solvent to form metal-centered nanoparticles according to the invention, as described above.

An exemplary Cu@Si nanoparticle preparation is now described.

10 All operations up to the addition of water were conducted in an inert atmosphere (nitrogen gas). Triglyme (~50 mL) was freshly distilled from sodium metal under nitrogen and was added to a clean, dry Schlenk flask (250 mL). To the flask was added copper(II) acetate monohydrate (1.0059 g: 5.0384 mmol), sodium metal (0.19 g: 8.3 mmol) and a magnetic stirbar. Stirring was initiated, and the mixture was
15 heated to reflux. The copper acetate quickly dissolved to produce a clear, light-green solution. Over a period of one hour, the solution changed color from light green to dark green and finally brown. The flask was then cooled in an icebath, and silicon tetrachloride (0.58 mL: 5.1 mmol) was added. The mixture was again heated to reflux and maintained for two hours. During that time the solution changed to a
20 cloudy-pink color, and a gray precipitate was observed to form. The heat source was then removed and stirring ceased. The clear supernatant solution was observed to luminesce when irradiated with a hand-held UV lamp (irradiation ~365 nm). Stirring was resumed, and a diethyl solution of methyl lithium was slowly added to the mixture, which changed to a pea-green color upon addition. The
25 mixture was heated to reflux for a period of one hour during which it changed to a purple color. Water (20 mL: 1.1 mol) was slowly added with no apparent reaction. The mixture was filtered through a 0.45 filter and the solids discarded. The solution was observed to luminesce when irradiated with a hand-held UV lamp (irradiation ~365 nm). A drop of the solution was placed onto a copper grid and submitted for
30 analysis by TEM spectroscopy. Irregularly shaped clusters of silicon (~40 nm) were clearly visible in the TEM images which contained small copper clusters (~7 nm).

which appeared as black spots in an otherwise gray mass (silicon-gray, copper-black).

In the nanoparticles of the invention, the physics and chemistry of the individual clusters will be largely affected by either quantum confinement of valence
5 electrons and quasiparticles (excitons, plasmons) or by surface defects. A Schottky barrier may occur at the metal-silicon interface that may significantly influence the properties of the silicon shell and the particle as a whole. The M@Si particle may be electrically polarized leading to a charged outer surface with chemical and optical
10 properties distinct from Si-only clusters.

CLAIMS

I claim:

1. A method for preparing silicon-containing particles, comprising the steps of:
 - a) reducing a halosilane with a metal in a solvent to form a first reaction mixture containing a metal halide, amorphous silicon and halogenated silicon nanoparticles;
 - b) permitting the first reaction mixture to stand for a sufficient time to form a second reaction mixture including larger particles based on the halogenated silicon nanoparticles;
 - c) hydrolyzing the larger particles formed in step b with water to form a third reaction mixture containing a haloacid and hydrolyzed silicon nanoparticles; and
 - d) passivating the larger particles formed in step b with an organic Grignard reagent to form a fourth reaction mixture including a metal halide salt and organic passivated silicon nanoparticles.
2. A method according to claim 1, wherein the metal is a member selected from the group consisting of Group I and Group II metals of the Periodic Table and transition metals.
3. A method according to claim 1, wherein the halosilane is a compound selected from the group consisting of a silane of Br, Cl, I, or F and an organosilane of Br, Cl, I or F, where R is any organic group that can bond to Si.
4. A method according to claim 1, wherein step a takes place under reflux conditions for the solvent.
5. A method according to claim 1, wherein step b occurs at room temperature.
6. A method according to claim 3, wherein halosilane is SiCl_4 .

7. A method according to claim 1, wherein the metal is sodium.

8. A method according to claim 1, wherein step b occurs at a temperature about room temperature.

5

9. A method according to claim 1, wherein the duration of step b is about 24 hours.

10. A method according to claim 1, wherein the solvent is an organic solvent.

10 11. A method according to claim 10, wherein the organic solvent is a coordinating solvent.

12. A method according to claim 1, wherein the solvent is selected from the group consisting of diglyme, triglyme, tetraglyme, diethyl ether and tetrahydrofuran and
15 mixtures thereof.

13. A method according to claim 1, wherein the solvent includes a nonpolar solvent.

14. A method according to claim 1, wherein the third reaction mixture contains
20 $\text{Si}_{20}(\text{OH})_{20}$ monomer.

15. A method according to claim 1, wherein the third reaction mixture contains dimers of $\text{Si}_{20}(\text{OH})_{20}$.

25 16. A method according to claim 1, wherein the third reaction mixture contains trimers of $\text{Si}_{20}(\text{OH})_{20}$.

17. A method according to claim 1, wherein the Grignard reagent is RLi or R_2Mg .

30 18. A method according to claim 1, wherein steps a, b, c and d occur in an inert environment.

19. A silicon nanoparticle prepared according to the method of claim 1.

20. A silicon nanoparticle prepared according to claim 1 having a particle diameter of less than about 100 nm.

5

21. A silicon nanoparticle according to claim 19 having a particle diameter of between about 0.5 and 10 nm.

10

22. A light emitting device, comprising silicon nanoparticles having the formula $\text{Si}_{20}(\text{OH})_{20}$ or polymers thereof.

23. A semiconductor device, comprising silicon nanoparticles having the formula $\text{Si}_{20}(\text{OH})_{20}$ or polymers thereof.

15

24. A method for preparing silicon-containing particles, comprising the steps of:

a) reducing a halosilane with a metal under reflux in a solvent to form a first reaction mixture containing a metal halide, amorphous silicon and halogenated silicon nanoparticles;

20

b) permitting the second reaction mixture to stand for a sufficient time to form a second reaction mixture including larger particles based on the halogenated silicon nanoparticles;

c) hydrolyzing the larger particles formed in step b with an alcohol to form a third reaction mixture including a haloacid and alkoxy passivated silicon nanoparticles; and

25

d) passivating the larger particles formed in step b with an organic Grignard reagent to form a fourth reaction mixture including a metal halide salt and organic passivated silicon nanoparticles.

30

25. A method according to claim 23, wherein the metal is a member selected from the group consisting of Group I and Group II metals of the Periodic Table and transition metals.

26. A method according to claim 23, wherein the halosilane is a compound selected from the group consisting of a silane of Br, Cl, I, or F and an organosilane of Br, Cl, I or F, where R is any organic group that can bond to Si.

5 27. A method according to claim 23, wherein the halosilane is SiCl_4 .

28. A method according to claim 24, wherein the metal is sodium.

29. A method according to claim 23, wherein step b occurs at a temperature about
10 room temperature.

30. A method according to claim 23, wherein the duration of step b is about 24 hours.

15 31. A method according to claim 23, wherein the solvent is an organic solvent.

32. A method according to claim 30, wherein the organic solvent is a coordinating solvent.

20 33. A method according to claim 30, wherein the solvent is selected from the group consisting of diglyme, triglyme, tetraglyme, diethyl ether and tetrahydrofuran and mixtures thereof.

34. A method according to claim 1, wherein the solvent includes a nonpolar solvent
25 in a mixture.

35. A method according to claim 23, wherein the third reaction mixture contains $\text{Si}_{20}(\text{OH})_{20}$ monomer.

30 36. A method according to claim 23, wherein the third reaction mixture contains dimers of $\text{Si}_{20}(\text{OH})_{20}$.

37. A method according to claim 23, wherein the third reaction mixture contains trimers of $\text{Si}_{20}(\text{OH})_{20}$.

38. A method according to claim 23, wherein the Grignard reagent is RLi or R_2Mg .

5

39. A method according to claim 23, wherein steps a, b, c and d occur in an inert environment.

40. A silicon nanoparticle prepared according to the method of claim 23.

10

41. A silicon nanoparticle prepared according to claim 23 having a particle diameter of less than about 100 nm.

15

42. A silicon nanoparticle according to claim 40 having a particle diameter of between 0.5-10 nm.

43. A light emitting device, comprising silicon nanoparticles having the formula $\text{Si}_{20}(\text{OH})_{20}$ or polymers thereof.

20

44. A semiconductor device, comprising silicon nanoparticles having the formula $\text{Si}_{20}(\text{OH})_{20}$ or polymers thereof.

45. A method for preparing a metal-centered silicon nanoparticle, comprising the steps of:

25

a) reducing a metal salt with a metal reductant in a solvent, optionally containing a chelating ligand, to form a first reaction mixture containing metal clusters;

b) reacting the metal clusters with a halosilane to form a second reaction mixture containing halogenated metal clusters coated with a silicon film;

c) permitting the second reaction mixture to stand for a sufficient time to form a third

30

reaction mixture including larger particles based on the halogenated metal-centered silicon nanoparticles;

d) hydrolyzing the larger particles formed in step c with water to form a fourth reaction mixture containing a haloacid and hydrolyzed metal centered silicon nanoparticles; and

5 e) passivating the larger particles formed in step c with an organic Grignard reagent to form a fifth reaction mixture including a metal halide salt and organic passivated metal-centered silicon nanoparticles.

10 46. A method according to claim 44, wherein the metal is a member selected from the group consisting of Group I and Group II metals of the Periodic Table and transition metals.

15 47. A method according to claim 44, wherein the halosilane is a compound selected from the group consisting of a silane of Br, Cl, I, or F and an organosilane of Br, Cl, I or F, where R is any organic group that can bond to Si.

48. A method according to claim 44, wherein the halosilane is SiCl_4 .

49. A method according to claim 44, wherein the metal is sodium.

20 50. A method according to claim 44, wherein step b occurs at a temperature about room temperature.

51. A method according to claim 44, wherein the duration of step b is about 24 hours.

25 52. A method according to claim 44, wherein the solvent is an organic solvent.

53. A method according to claim 51, wherein the organic solvent is a coordinating solvent.

30

54. A method according to claim 44, wherein the solvent is selected from the group consisting of diglyme, triglyme, tetraglyme, diethyl ether and tetrahydrofuran and mixtures thereof.

5 55. A method according to claim 44, wherein the solvent includes a nonpolar solvent in a mixture.

56. A method according to claim 44, wherein the third reaction mixture contains $\text{Si}_{20}(\text{OH})_{20}$ monomer.

10

57. A method according to claim 44, wherein the third reaction mixture contains dimers of $\text{Si}_{20}(\text{OH})_{20}$.

15

58. A method according to claim 44, wherein the third reaction mixture contains trimers of $\text{Si}_{20}(\text{OH})_{20}$.

59. A method according to claim 44, wherein the Grignard reagent is RLi or R_2Mg .

20

60. A method according to claim 44, wherein steps a, b, c and d occur in an inert environment.

61. A silicon nanoparticle prepared according to the method of claim 44.

25

62. A silicon nanoparticle according to claim 44 having a particle diameter of less than about 100 nm.

63. A silicon nanoparticle according to claim 61 having a particle diameter of between 0.5-10 nm.

30

64. A light emitting device, comprising silicon nanoparticles having the formula $\text{Si}_{20}(\text{OH})_{20}$ or polymers thereof.

65. A semiconductor device, comprising silicon nanoparticles having the formula $\text{Si}_{20}(\text{OH})_{20}$ or polymers thereof.

66. A method for preparing a metal-centered silicon nanoparticle, comprising the steps of:

a) reducing a metal salt with a metal reductant in an organic solvent, optionally containing a chelating ligand, to form a first reaction mixture containing metal clusters;

b) reacting the metal clusters with a halosilane to form a second reaction mixture containing halogenated metal clusters coated with a silicon film;

c) permitting the second reaction mixture to stand for a sufficient time to form a third reaction mixture including larger particles based on the halogenated metal-centered silicon nanoparticles;

d) hydrolyzing the larger particles formed in step c with an alcohol to form a fourth reaction mixture including a haloacid and alkoxy passivated silicon nanoparticles; and

e) passivating the larger particles formed in step c with an organic Grignard reagent to form a fifth reaction mixture including a metal halide salt and organic passivated metal-centered silicon nanoparticles.

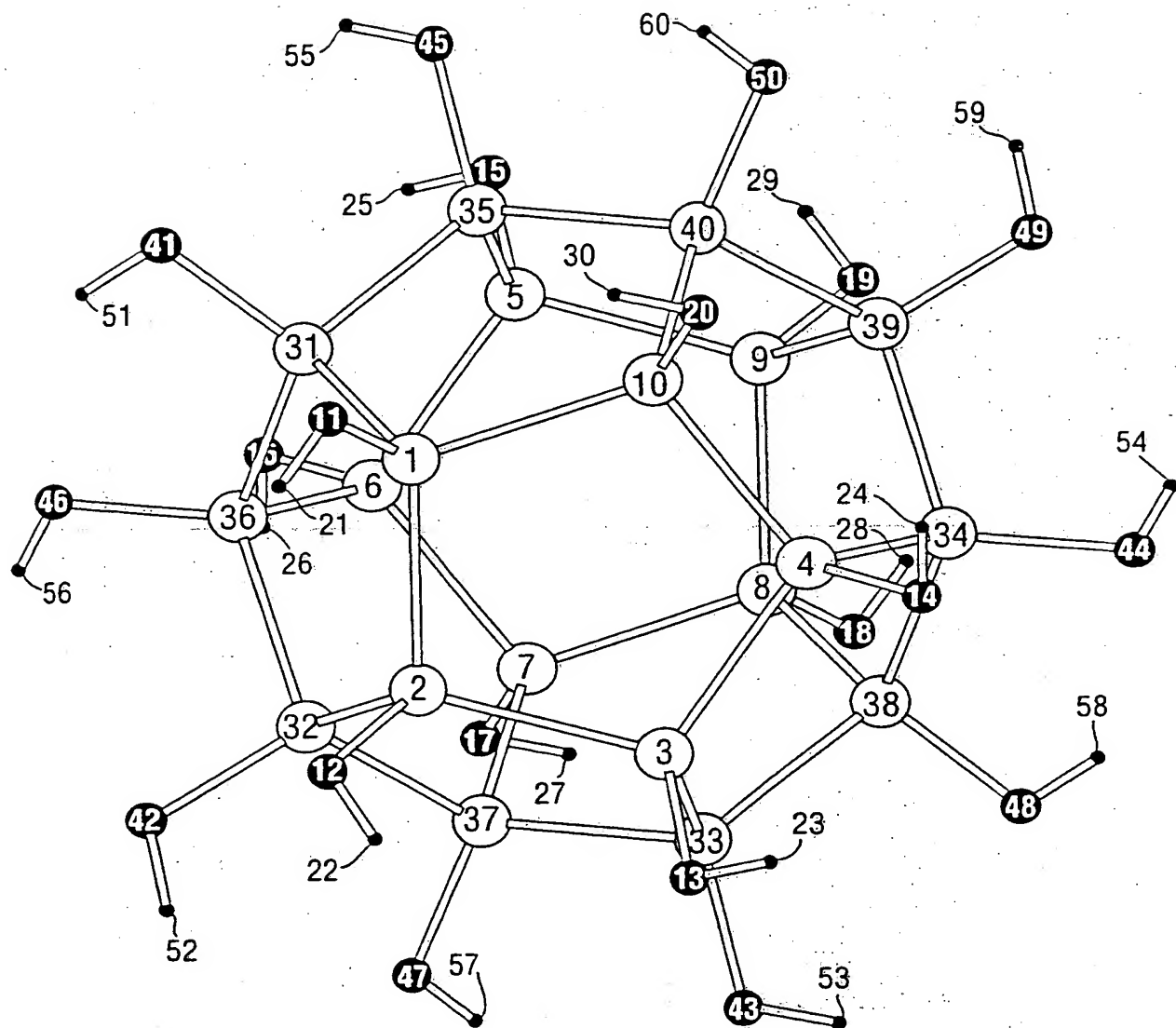


FIG. 1

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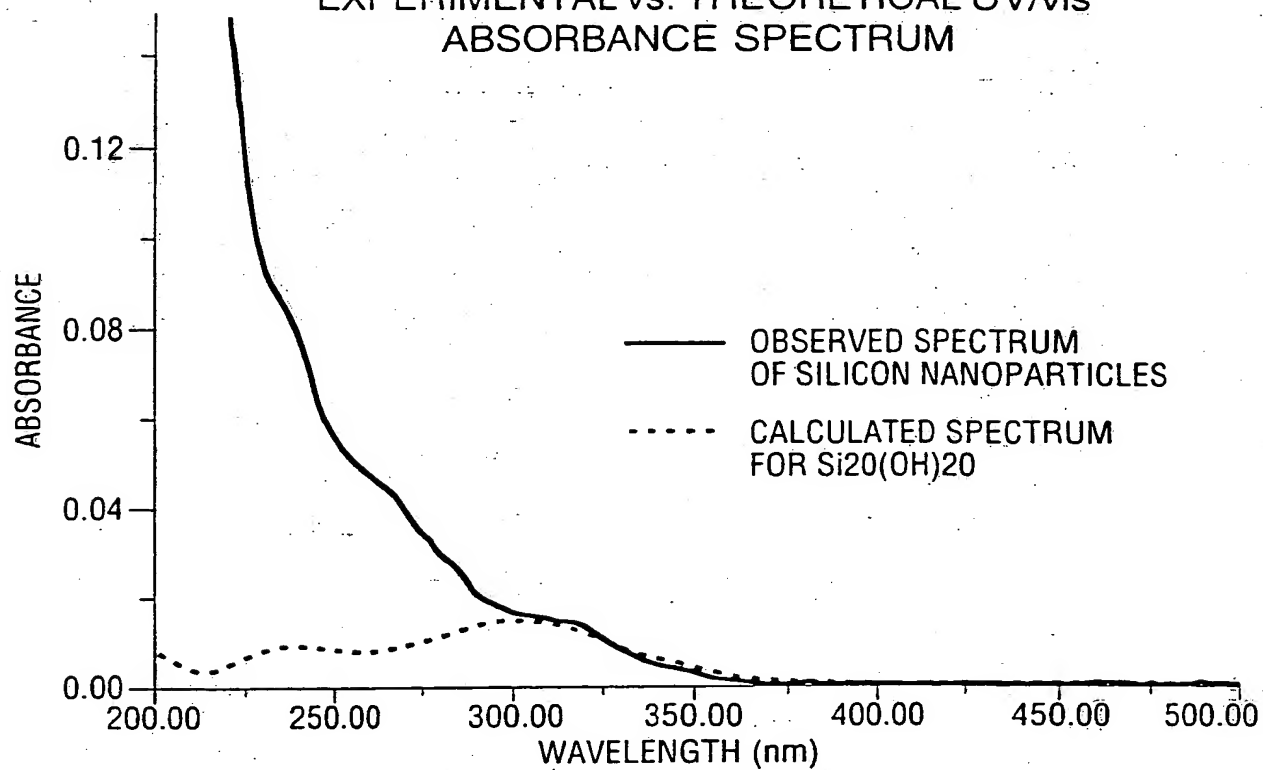
EXPERIMENTAL vs. THEORETICAL UV/vis
ABSORBANCE SPECTRUM

FIG. 2

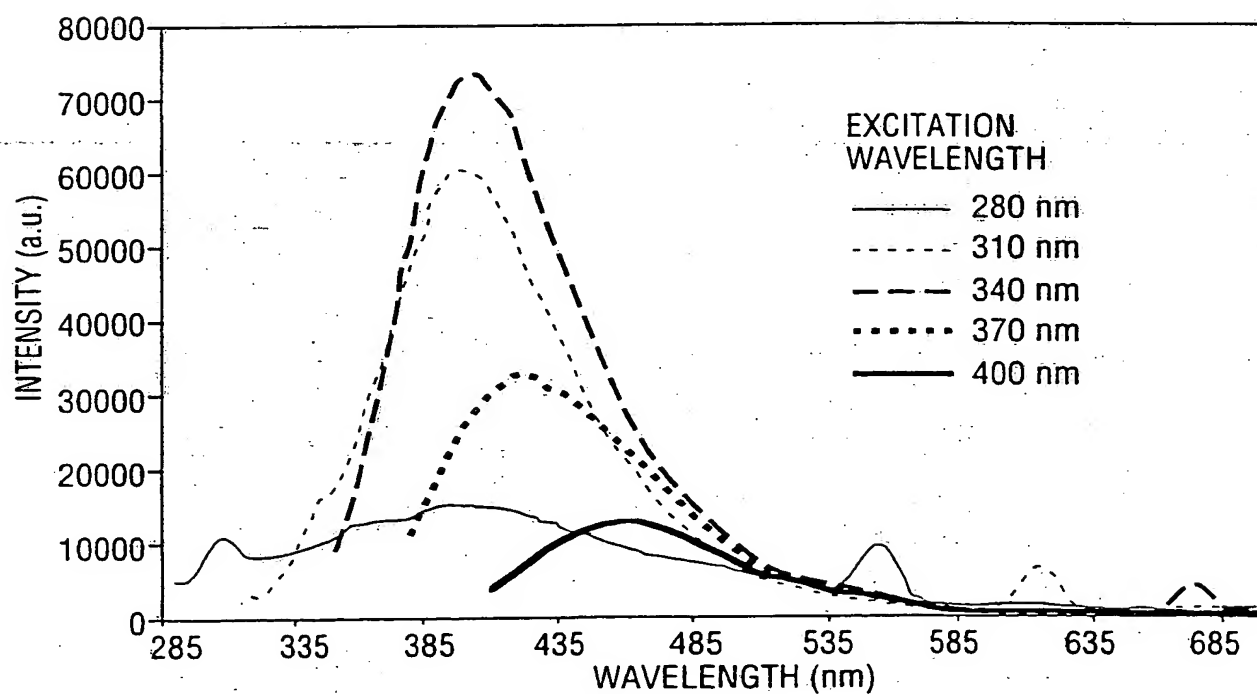


FIG. 3

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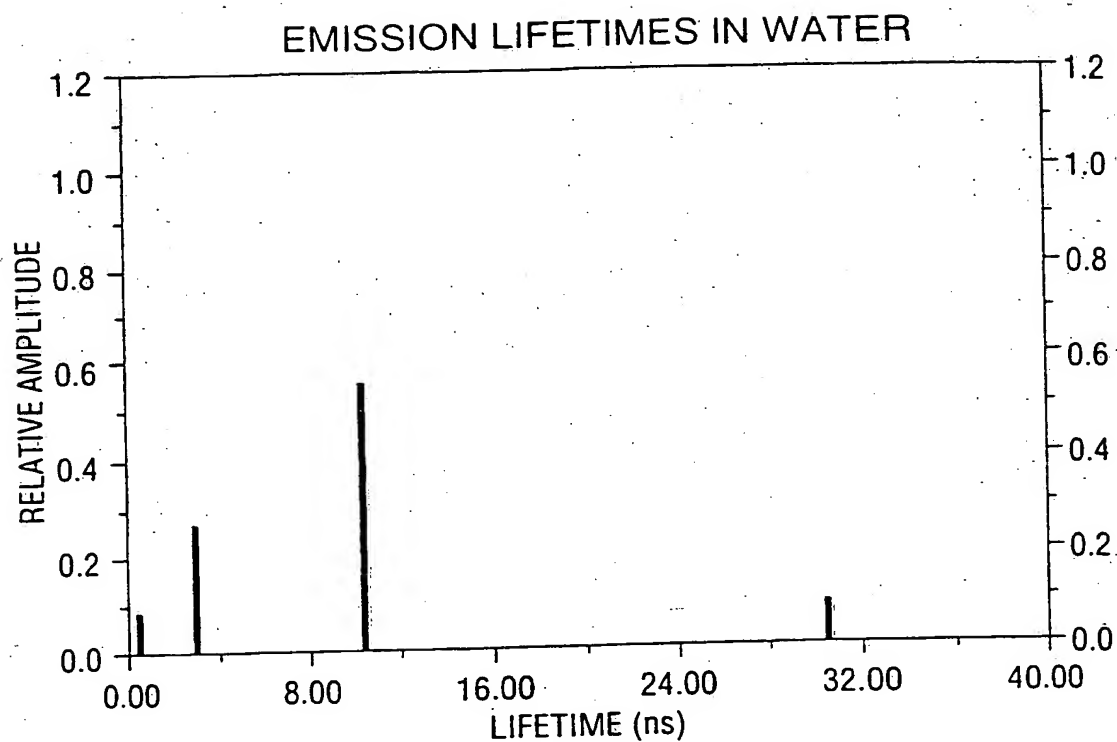


FIG. 4

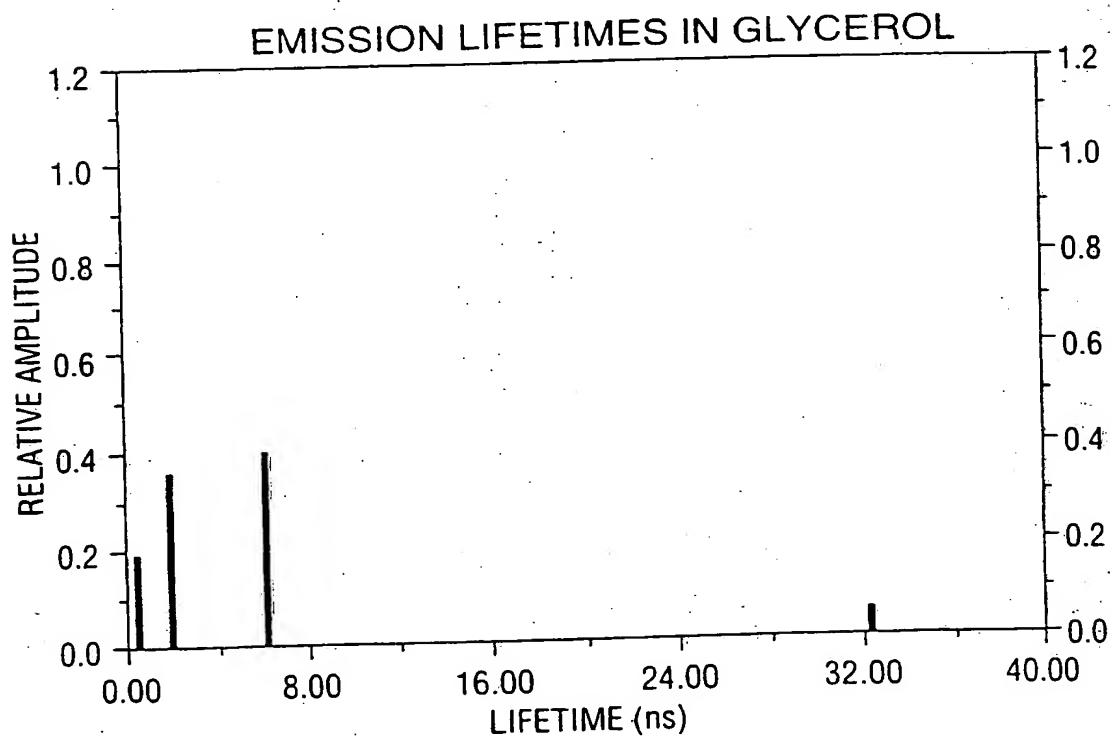


FIG. 5

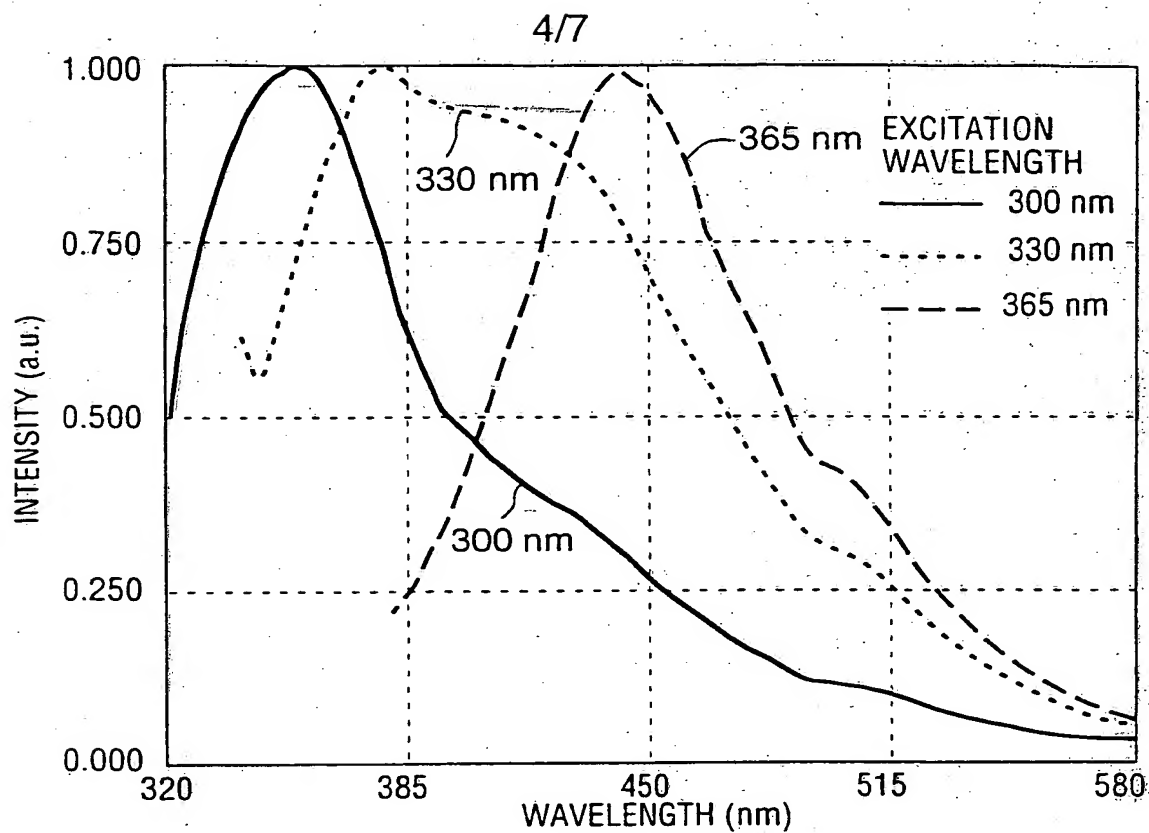


FIG. 6A

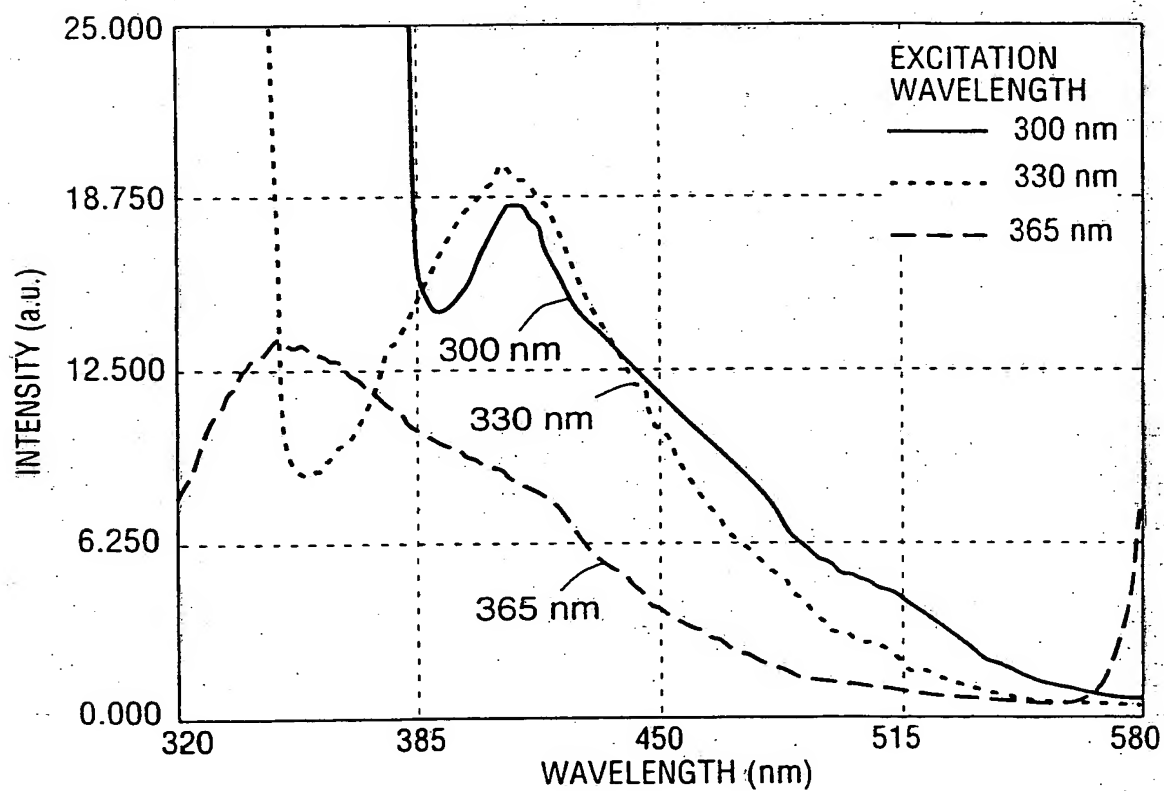


FIG. 6B

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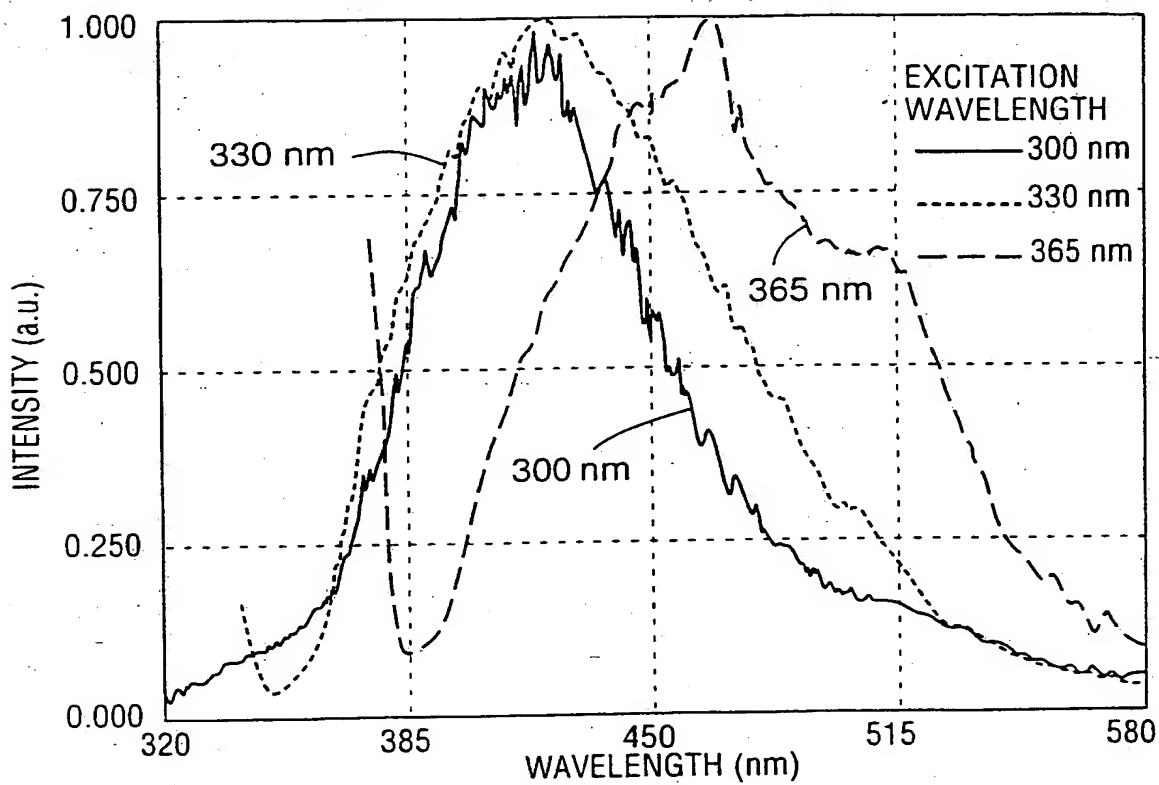


FIG. 6C

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FIG. 7

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PARALLEL EELS Si-K SPECTRUM

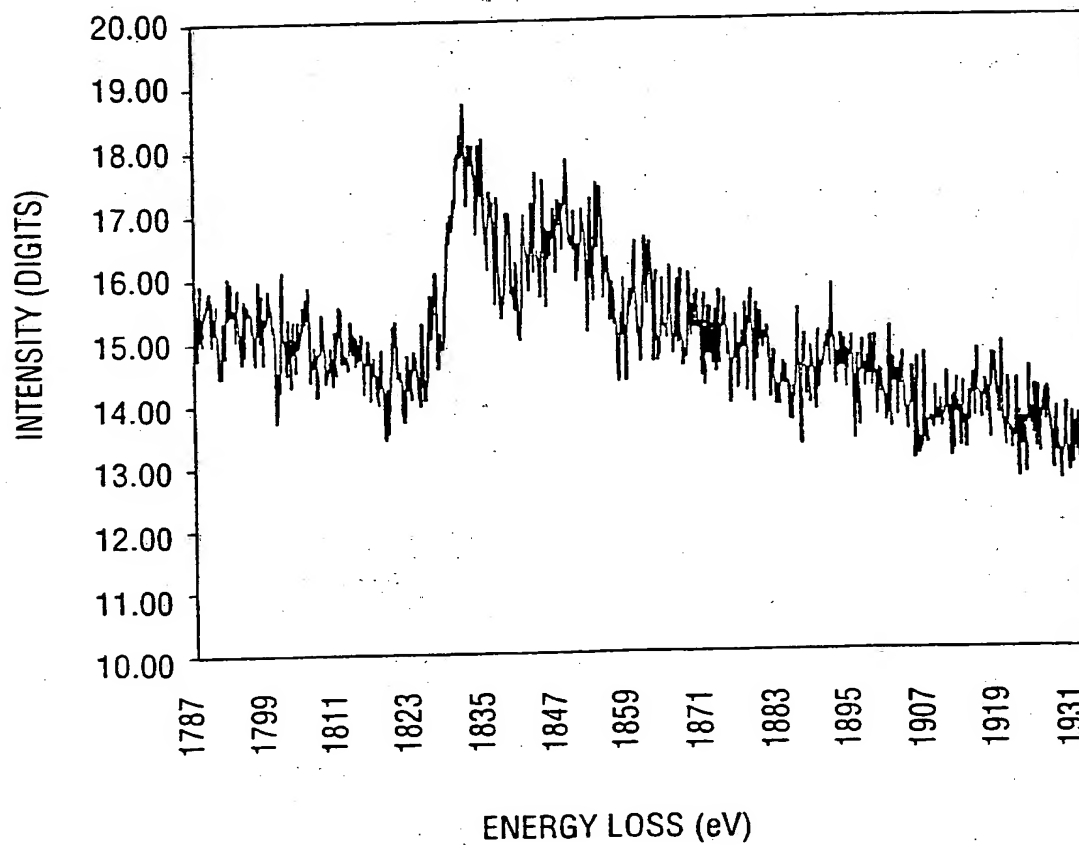


FIG. 8

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(74) Agents: COLEMAN-JAMES, Patricia et al.; Mc-
Cutchen, Doyle, Brown & Enersen, LLP, Three Embar-
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SITY OF HAWAII [US/US]; 2800 Woodlawn Drive, Suite
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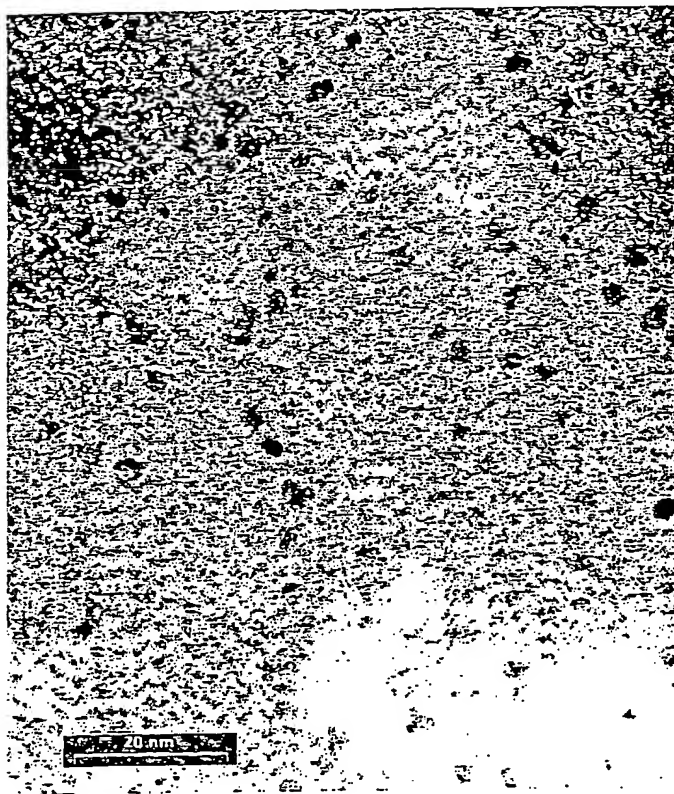
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(72) Inventor; and

(75) Inventor/Applicant (*for US only*): HARWELL, David

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ning of each regular issue of the PCT Gazette.*

(54) Title: SYNTHESIS OF SILICON NANOPARTICLES AND METAL-CENTERED SILICON NANOPARTICLES AND AP-
PLICATIONS THEREOF



(57) Abstract: IPCicon nanoparticles and metal-cen-
tered silicon nanoparticles and solution phase methods
of synthesis using commonly available reagents
and ordinary conditions. Solvent may be diglyme,
triglyme, tetraglyme, even in mixture with nonpolar
solvent. A halosilane is reduced with metal, for
example, at reflux conditions. Reaction product is
hydrolyzed or passivated to produce stable subunit that
can agglomerate or polymerize into larger structures.
Particle size synthesized can be controlled. These
particles and structures are photoluminescent and
suitable for various applications, including light
emitting devices.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HEATH J R: "A liquid-solution-phase synthesis of crystalline silicon" SCIENCE, 13 NOV. 1992, USA, vol. 258, no. 5085, pages 1131-1133, XP002159943 ISSN: 0036-8075 cited in the application the whole document	1-3,6,7, 13, 19-21, 24-28, 34, 40-42, 45,66
A	EP 0 194 816 A (KEMIRA OY) 17 September 1986 (1986-09-17) claims 1-10	1

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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PCT/US 00/23132

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International Application No

PCT/US 00/23132

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			US 6157047 A	05-12-2000

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- (72) Inventor; and
(75) Inventor/Applicant (*for US only*): HARWELL, David [US/US]; 3029 Lowrey Avenue, J31008, Honolulu, HI 96822 (US).
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- (71) Applicant (*for all designated States except US*): UNIVERSITY OF HAWAII [US/US]; 2800 Woodlawn Drive, Suite 280, Honolulu, HI 96822 (US).
- Published:
— with international search report

[Continued on next page]

(54) Title: SYNTHESIS OF SILICON NANOPARTICLES AND METAL-CENTERED SILICON NANOPARTICLES AND APPLICATIONS THEREOF



(57) Abstract: IPCicon nanoparticles and metal-centered silicon nanoparticles and solution phase methods of synthesis using commonly available reagents and ordinary conditions. Solvent may be diglyme, triglyme, tetraglyme, even in mixture with nonpolar solvent. A halosilane is reduced with metal, for example, at reflux conditions. Reaction product is hydrolyzed or passivated to produce stable subunit that can agglomerate or polymerize into larger structures. Particle size synthesized can be controlled. These particles and structures are photoluminescent and suitable for various applications, including light emitting devices.

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